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(71)Applicant : JAPAN STORAGE BATTERY CO  
LTD

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(72)Inventor : SAITO SATORU

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(54) DIRECT TYPE METHANOL FUEL CELL HAVING SOLID POLYMER ELECTROLYTE

(57)Abstract:

PROBLEM TO BE SOLVED: To reduce a crossover of methanol and to prevent drop in catalytic activity of a positive electrode by including a mixed solution of alcohol other than methanol and water in a solid polymer electrolyte.

SOLUTION: A catalyst dispersion solution is applied to the surface of carbon paper which is water repellent treated, and air dried to form a catalyst layer on one side of the carbon paper to form a positive electrode and a negative electrode. A Nafion (R) 115 film is interposed between the positive electrode and the negative electrode, so that the surface of the catalyst is faced to the Nafion film, and they are jointed with a hot press to form an electrode/electrolyte film jointed body. Air is supplied to the positive electrode and an aqueous methanol solution is supplied to the negative electrode to regulate the movement of methanol to the mixed solvent layer in a solid polymer electrolyte, the solubility of the methanol contained in the solvent of the solid polymer electrolyte is kept low, and the amount of the methanol reaching the positive electrode is made small. As a result, the catalytic activity of the positive electrode is kept in the original state, and the deterioration in battery characteristics is prevented.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the direct mold methanol fuel cell which supplies a methanol to a negative electrode, is made to carry out direct electrochemical reaction with a negative electrode, and obtains power.

[0002]

[Description of the Prior Art] A fuel cell is a cell which equips with two electrodes the both sides of the electrolyte which is an ionic conductor, supplies oxidation gas (oxidizer), such as oxygen and air, to one electrode, supplies fuels (reducing agent), such as hydrogen and a hydrocarbon, to the electrode of another side, is made to cause electrochemical reaction, and is made to generate the electrical and electric equipment.

[0003] Although there are many classes of fuel cells A direct mold methanol fuel cell (it abbreviates to DMFC) Supply the methanol which is a fuel to a direct negative electrode, and it compares with using the hydrogen in which many fuel cells reformed hydrogen or a hydrocarbon as a fuel. It is thought equipment is not only easy, but that it is most suitable for small and portability since transportation of the fuel itself is also easy and it may moreover be able to operate at the temperature of 100 degrees C or less, and it is seen as a hopeful as a future source for automobiles of power.

[0004] As an electrolyte of a direct mold methanol fuel cell, it changes from an early alkali mold to an acid type, and, recently, the solid-state polyelectrolyte is used. By using a solid-state polyelectrolyte, operating temperature could be made higher than the case of a liquid electrolyte, and, as for the engine performance of a direct mold methanol fuel cell, the thing twist remarkable improvement of the first stage was carried out.

[0005] The direct mold methanol fuel cell (PEM-DMFC) which used the solid-state polyelectrolyte is Du. It has the structure which sandwiched the both sides of a proton conductivity solid-state polyelectrolyte like Nafion made from Pont with two porous electrodes which attached the catalyst, a methanol is directly supplied to a negative electrode, and oxygen or air is supplied to a positive electrode. In a negative electrode, a methanol and water react, a carbon dioxide, a proton, and an electron are generated, and an electron reaches a positive electrode, after working through an external circuit. Moreover, a proton reaches [ be / it / under / solid polymer electrolyte / passing ] a positive electrode. In a positive electrode, oxygen, a proton, and an electron react and water generates. Therefore, the overall reaction of a direct mold methanol fuel cell is a reaction which water and a carbon dioxide generate from a methanol and oxygen. These reactions borrow the assistance of the catalyst in an electrode, and advance. Although the theoretical electrical potential difference of this reaction is 1.18V, it turns into a low electrical potential difference from this value in an actual cell for IR drop etc.

[0006] The direct mold methanol fuel cell has the fault that the output and effectiveness of a cell are low, as compared with other fuel cells, although the property has improved considerably. [M. to which it is clear that that cause has the low activity of the catalyst which oxidizes a methanol, and that it is two of the short passes (this phenomenon is called "the crossover") that then, a methanol diffuses the inside of

an electrolyte, arrives at an anode plate, and carries out a direct reaction to an oxidizing agent on the catalyst of a positive electrode It is P.Hogarth and H.A.Hards Platinum Metals Rev.40(4) 150 (1996)]. [0007] In a direct mold methanol fuel cell, although a positive electrode and a negative electrode are required for a catalyst, especially the catalyst of a negative electrode is a problem. Namely, [R. to which the carbon monoxide which stuck to platinum arises, this carries out poisoning of the platinum, and catalytic activity is reduced when a methanol oxidizes on a platinum catalyst Parsons and T.Vandermoot J.Electroanal.Chem., 257 9(1988)]. In order to remove a carbon monoxide from the front face of platinum you to be Sumiya, addition of a secondary metal is considered and it is known for current that a platinum-ruthenium system is a high activity catalyst most. [0008] Although the ion-exchange-membrane resin film as a solid-state polyelectrolyte does not show conductivity at all by dryness, it comes to show high conductivity by making it usually swell with water.

[0009] Du known best as a solid-state polyelectrolyte The structure of the Nafion film of Pont The water-repellent poly fluoro ethylene  $[-(CF_2)_n-]$  frame part which is a principal chain, It consists of a part of the sulfonic acid group  $(-SO_3H)$  which is an ion exchange group of a hydrophilic property. When this film absorbs water, the parts of the ion exchange group of a hydrophilic property gather. The model that form a spherical cluster and this cluster is distributing in the matrix of poly fluoro ethylene is leading. In this model [considered that water is contained into a cluster part and tied with the path where these clusters are thin -- Takenaka carpenter \*\*\*\*\* 36 81(1985)]. It is thought that it is having same structure also in other solid-state polyelectrolytes.

[0010]

[Problem(s) to be Solved by the Invention] If a methanol contacts the solid polymer electrolyte which absorbed water, since a methanol tends to melt into water, it will dissolve in the water in the cluster in a solid polymer electrolyte, will reach [ be / it / under / of it / passing ] a positive electrode, and will oxidize on the catalyst of a positive electrode.

[0011] On the other hand, in order that the noble metals as a catalyst may oxidize electrochemically the methanol which has passed along the inside of an electrolyte from the negative electrode in a positive electrode, the property of a positive electrode gets remarkably bad. Although the approach of considering as the phenomenon in which a methanol reaches [ be / it / under / electrolyte / passing ] a positive electrode, and the method of decreasing the so-called crossover, and making the pressure of oxygen or air high, and the approach of raising the operating temperature of a cell to 100 degrees C or more were examined and the property has improved considerably, sufficient property is not acquired practical. Moreover, in order to make the pressure of oxygen or air high, and in order to raise the operating temperature of a cell, the equipment for it is needed and it becomes complicated as the whole cell.

[0012] what is necessary is to make it as small as possible that the methanol which is a fuel reaches a positive-electrode side through a solid-state polyelectrolyte, i.e., the crossover of a methanol, or just to lose, in order to improve the property of a direct mold methanol fuel cell -- being deep -- it is clear and the concrete means for it was searched for.

[0013]

[Means for Solving the Problem] This invention includes alcohol other than a methanol, and the mixed solution of water in a solid-state polyelectrolyte in the direct mold methanol fuel cell which used the solid-state polyelectrolyte.

[0014]

[Embodiment of the Invention] The direct mold methanol fuel cell which used the solid-state polyelectrolyte which becomes this invention joins the porous electrode which attached the catalyst bed in the both sides of a proton conductivity solid-state polyelectrolyte, to a negative electrode, supplies oxygen or hydrogen for the mixture of a methanol and water to a positive electrode, and takes out the electrical and electric equipment.

[0015] As a base of a porous electrode, forward and a negative electrode can give a water-repellent finish and use porous bases, such as a Plastic solid of carbon paper and carbon, a sintered compact of

carbon, a sintered metal, and a foam metal, and polytetrafluoroethylene etc. can be used as water repellent.

[0016] As a precious metal catalyst, for positive electrodes, platinum, a platinum alloy, gold, a gold alloy, palladium, a palladium alloy, etc. can use alloys, such as platinum or platinum, a ruthenium and gold, and a rhenium, for negative electrodes, and the carbon powder which supported the impalpable powder of these noble metals or noble metals can be used.

[0017] The porous electrode which becomes this invention applies a catalyst distribution solution to the front face of the water-repellent electrode, and is produced. Therefore, a catalyst distribution solution is produced to mix to homogeneity the solid-state polyelectrolyte which dissolved in alcohol etc. with the carbon powder which supported the particle of a catalyst or catalyst of platinum black etc., and water repellent in a suitable solvent.

[0018] Moreover, as a solid-state polyelectrolyte used for a direct mold methanol fuel cell, various ion-exchange-membrane resin, such as perfluorocarbon sulfonic acid system resin and styrene-divinylbenzene copolymer system resin, can be used.

[0019]

[Example] The structure and the property of a direct mold methanol fuel cell which become this invention are explained in full detail using a suitable example.

[0020] The direct mold methanol fuel cell which made water and 2-propanol \*\* contain in a [example 1] solid-state polyelectrolyte was produced.

[0021] First, carbon paper with a% [ of voidage ] of 75 and a thickness of 0.40mm is turned off in 50mmx50mm magnitude, it washes by 2-propanol, and after being immersed for several seconds into 20 percent-by-weight \*\*\*\* dispersion polytetrafluoroethylene water solution, taking out polytetrafluoroethylene and seasoning naturally it, 300 degrees C of dry things are calcinated for 10 minutes under an argon gas ambient atmosphere. In the obtained given a water-repellent finish a water-repellent finish carbon paper, it is 2 about 3mg/cm. Polytetrafluoroethylene is attached.

[0022] Next, a catalyst distribution solution is produced. First, 5g of platinum support carbon which contains platinum 10% of the weight is put into the beaker made from stainless steel, and 80ml of water is added and agitated, and 2-propanol 80ml is added further and it agitates for 1 hour. Next, polytetrafluoroethylene was added 2ml of 20 percent-by-weight \*\*\*\* dispersion polytetrafluoroethylene water solutions, and was agitated, in addition, it agitated with the agitator for 1 hour, irradiating a supersonic wave, and the catalyst distribution solution for positive electrodes was produced further 10ml (made in [ which is included 5 % of the weight of Nafion ] Aldrich Chemical) of commercial Nafion solutions.

[0023] Using 10g for the platinum-ruthenium support carbon containing 10 % of the weight of platinum, and 10 % of the weight of rutheniums independently, others are the same procedures as the object for positive electrodes, and produced the catalyst distribution solution for negative electrodes.

[0024] The positive electrode and the negative electrode applied and seasoned naturally the catalyst distribution solution on the front face of carbon paper [ finishing / a water-repellent finish ], respectively. Furthermore, it dried at 110 degrees C after spreading and an air drying again for 1 hour, and the electrode for direct mold methanol fuel cells with which the catalyst bed was attached in one side was obtained. In addition, for the thickness of the catalyst bed of the electrode for positive electrodes, about 0.05mm and the amount of platinum of an electrode surface are about 1.0 mg/cm<sup>2</sup>. Carrying out, for the thickness of the catalyst bed of the electrode for negative electrodes, about 0.08mm and the amount of platinum of an electrode surface are about 2.0 mg/cm<sup>2</sup>. \*\*.

[0025] Thus, between the obtained object for positive electrodes, and the electrode for negative electrodes, by inserting, as the field in which the catalyst of an electrode was attached is on the Nafion side, the hotpress of the 140 degrees C of the Nafion 115 film as a solid-state polyelectrolyte was carried out for 3 minutes, it was joined, and the electrode / electrolyte membrane zygote was produced.

[0026] An electrode / electrolyte zygote is beforehand immersed in the water solution containing the 2-propanol of 8 percentage by weight, and the interior of the Nafion film is filled with the direct mold methanol fuel cell (it considers as Cell A) which becomes this invention in the water solution of 2-

propanol. On the other hand, the direct mold methanol fuel cell for a comparison (it considers as Cell B) fills the interior of the Nafion film with water as usual.

[0027] Next, the water solution which includes air in a positive electrode and includes a methanol in a negative electrode 1mol/l was supplied, and the property of a direct mold methanol fuel cell was measured. Drawing 1 is what showed the i-V curve, and the property of the cell A which becomes this invention became what was considerably excellent compared with the conventional cell B.

[0028] A [example 2] electrode / electrolyte zygote is immersed in the water solution containing the 1-butanol of 7 percent by weight, the interior of the Nafion film is filled with the water solution of 1-butanol, and other conditions produced the same direct mold methanol fuel cell (it considers as Cell C) as an example 1. As a result of measuring the i-V curve of Cell C, it was almost the same as the property of Cell A.

[0029]

[Effect of the Invention] Although the water solution which melted the methanol as a fuel to the negative electrode is supplied in a direct mold methanol fuel cell, when the solid polymer electrolyte with which the methanol which is a fuel absorbed water is contacted and only water is contained in the solid polymer electrolyte, it will mix with water promptly, and a methanol will diffuse the inside of the water contained in a solid polymer electrolyte, will reach a positive electrode, and will react on the catalyst of a positive electrode. Consequently, the catalytic activity of a positive electrode falls and the property of a cell gets worse. However, like this invention, when the mixed solution of alcohol other than water and a methanol exists in a solid-state polyelectrolyte, the amount of the methanol which migration of the methanol to the mixed solvent phase in a solid polymer electrolyte is restricted, and the solubility of the methanol contained in the solvent in a solid polymer electrolyte is held at a small value, therefore reaches to a positive electrode becomes very little. Consequently, the catalytic activity of a positive electrode is maintained at the original condition, and can prevent degradation of a cell property. In addition, even if alcohol other than a methanol contacts the catalyst of a positive electrode, in order that it may not oxidize on a positive-electrode catalyst, a bad influence does not give the property of a positive electrode.

[0030] In addition, although 2-propanol and 1-butanol were used in the example as alcohol which dissolves in the water in a giant-molecule solid electrolyte, if the alcohol used in this invention dissolves in water, not only these but what kinds, such as monohydric alcohol, dihydric alcohol, and trihydric alcohol, of things are usable [ alcohol ].

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